# CERAMIC COATINGS FOR CONTROL OF REFLECTIVITY AND EMISSIVITY OF INCONEL

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## I. INTRODUCTION

Very little work has been done hitherto on the design of high-temperature coatings for controlling the emissive properties of refractory metals. The investigation described herein was done under contract with the Wright Air Development Division and had for its objective the development of two types of enamels with good adherence and fit to Inconel. One type of enamel was to have the highest possible emittance from moderate temperatures to approximately 1200° C. The second enamel was designed to give high reflectance to solar energy and high emittance in the infrared from moderate temperatures to 700° C or higher.

## II. PREPARATION OF MATERIALS

In order to formulate enamels of both types a frit developed by the National Bureau of Standards and designated by them as No. 332 was used as the base to which mill additions were made. It has the following composition:

| Oxide | % |
|---|---|
| $SiO_2$ | 37.5 |
| $B_2O_3$ | 6.5 |
| BaO | 44.0 |
| CaO | 3.5 |
| ZnO | 5.0 |
| $Al_2O_3$ | 1.0 |
| $ZrO_2$ | 2.5 |
| | 100.0 |

This frit has a sufficiently low coefficient of thermal expansion so that it will tolerate the solution of modifiers incorporated as mill additions and still maintain an expansion coefficient close to that of Inconel.

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The enamels designed to have high emittance were made up using the above frit together with mill additions of preformed black or nearly black spinels. In general, the spinels have low solubilities in silicate melts, and it was therefore anticipated that certain members of this family would provide the desired high emissivity in the low wavelength region where the silicate glasses have sharply decreased emissivities.

Six spinels consisting of combinations of cobalt or nickel oxide together with chromic, ferric, or manganic oxides were prepared by grinding the appropriate oxides together in a ball mill and then firing in alumina crucibles for 1 hour. Of these compositions, only that of $CoO.Cr_2O_3$ was heated to 1650° C; and the remainder were fired at 1370° C. X-ray examinations of the products showed the typical spinel structure.

For the preparation of coatings which were to have high reflectance in the visible and high emittance in the infrared, Frit 332 was opacified by ceric oxide, with stannic oxide, zirconium oxide, or magnesium oxide as auxiliary opacifiers.

Both the black and white enamels were prepared by wet grinding together a batch consisting of Frit 332, enameler's clay, opacifier, and water in accordance with procedures recommended by the National Bureau of Standards, except that the milling time was increased from 4 to 6 hours[1]. Surface preparation of the Inconel plates was by grit blasting with 80-mesh fused alumina grain. The enamels were applied by spraying, using a conventional spray gun. It was found advantageous to build up a thick coating by firing on several thin coats rather than by applying a thick coating followed by a single firing. The firing conditions were ordinarily 3-10 minutes at 1025° C but in some cases a higher temperature was required.

## III. MEASUREMENTS

The initial part of the work involved measurements of the total normal emittance of the coated specimens. Later the spectral emittance of selected specimens was determined. The apparatus used for this purpose has the following components:

1. A temperature control and measurement network (Figure 1) which supplies and controls the power delivered to the hollow Globar furnace used heating the enameled specimens.

2. A hollow Globar element (Figure 2) which contains both the blackbody cavity and a slot into which the enameled specimen is inserted.

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1. "Instructions for Preparing NBS Coating A418" issued by the National Bureau of Standards, February 8, 1951.

## TABLE I

### TOTAL NORMAL EMITTANCE AT VARIOUS TEMPERATURES OF BLACKBODY ENAMELS ON INCONEL

| Sample Designation | Spinel Component of Enamel* | Enamel Thickness Mils | Temp. °C | Total Normal Emittance |
|---|---|---|---|---|
| B-7 | $CoO.Cr_2O_3$ | 7.3 | 400 | 0.74 |
| B-7 | $CoO.Cr_2O_3$ | 7.3 | 700 | 0.74 |
| B-8 | $NiO.Cr_2O_3$ | 7.7 | 700 | 0.81 |
| B-9 | $NiO.Fe_2O_3$ | 8.1 | 700 | 0.80 |
| B-11 | $CoO.Fe_2O_3$ | 6.9 | 700 | 0.80 |
| B-12 | $CoO.Mn_2O_3$ | 2.0 | 400 | 0.87 |
| B-12 | $CoO.Mn_2O_3$ | 2.0 | 700 | 0.86 |
| B-12 | $CoO.Mn_2O_3$ | 2.0 | 1000 | 0.83 |
| B-12 | $CoO.Mn_2O_3$ | 6.9 | 400 | 0.83 |
| B-12 | $CoO.Mn_2O_3$ | 6.9 | 700 | 0.82 |
| B-12 | $CoO.Mn_2O_3$ | 6.9 | 1000 | 0.79 |
| B-13 | $CoO.Cr_2O_3$ | 5.2 | 400 | 0.76 |
| B-13 | $CoO.Cr_2O_3$ | 5.2 | 700 | 0.77 |

* All enamels except B-13 were made up of 60 parts of NBS Frit 332 and 40 parts of spinel; B-13 is a 50:50 mix of frit and spinel.

3. A radiation detection system (see Figure 3) collects infrared radiation from the blackbody cavity and the enameled sample. Figure 4 is a photograph of the assembly. Figure 5 shows a further view of the furnace. It consists of a tubular Globar element, of 3/4 inch ID and 1 1/8 inches OD, partially surrounded by layers of insulating brick which are held in place by a metal cage. The metal plate at the bottom of the furnace is free to rotate about the central axis of the Globar, so that the blackbody cavity and the surface of the coated sample may be viewed alternately. The table supporting the furnace can be leveled and adjusted vertically and, once it has been correctly positioned, the cavity and sample may be brought successively into the radiation detection system.

The blackbody cavity, the sample slot, and two small thermocouple holes were ultrasonically machined in the Globar to a tolerance of 1 mil. Specimens for emissivity measurements were 0.489 $\pm$ 0.001 inch long, 0.148 $\pm$ 0.001 inch wide, and 0.118 $\pm$0.0005 inch thick. The smaller tolerance on thickness was to insure that the surface of the enamel would be exactly flush with the outer surface of the Globar when it was inserted into the slot of the heating element. Thermocouples for the control of the heating element temperature and for measurement of cavity temperature were drilled through the hollow Globar so as to give a tight fit between the hole and the thermocouple insulator tubing. Another thermocouple for measuring the temperature of the enameled specimen was inserted in a small hole drilled half the length of the specimen and led up from the specimen by means of a trough machined in the Globar.

The emittance of the cavity was compared with that given by a Barnes high-temperature blackbody standard. Cavity temperature measurements were also made with a micro-optical pyrometer, as well as by probe thermocouples, and calibrations were thus obtained that take into account the thermal gradients which occur in the Globar.

## A. EMITTANCE OF BLACKBODY ENAMELS

The total normal emittances obtained for a group of blackbody enamels at various temperatures are given in Table I. The highest total emittance was obtained from the B-12 specimens, containing the enamel made from cobalt-manganese spinel which, at a thickness of 2.0 mils, has values of 0.87 to 0.83 in the temperature range from 400 to 1000$^{\circ}$ C. At a thickness of 6.9 mils the specimens coated with the B-12 enamel have emittances of 0.83 to 0.79. Values for the two B-12 enamel thicknesses are shown in Figure 6. The difference in emittance with coating thickness is, in part, a result of incomplete masking of the oxidized Inconel by the 2-mil coating. The result is, however, in contrast with total emittance values obtained by the National Bureau of Standards[1] in which it was shown that a 2-mil enamel coating on Inconel gave lower values than a 5-mil coating.

We believe that our higher emittance values for the thin coating are caused by formation of a layer of oxidized Inconel during the time that the specimens were held at temperature in making emittance measurements. Oxygen diffusion through the thin enamel undoubtedly occurs at high temperatures and, according to the National Bureau of Standards,[2] heavily oxidized Inconel has a total normal emittance of about 0.92 at 1127° C. At a thickness of 6.9 mils the emittance due to the metal is completely masked and the values given in Table I are probably those of the enamel itself.

In order to obtain indications of the refractoriness of the spinel-type coatings, a number of enameled Inconel plates were placed vertically in a furnace. All were heated at 1100° C for 30 minutes, then for 30 minutes at 1150° C, and finally for 30 minutes at 1200° C.

Enamel B-8, containing the nickel-chromium spinel, did not flow at 1150° C but after heating at 1200° C, followed by cooling to room temperature, it popped off the metal.

Enamel B-9, containing the nickel-iron spinel, did not flow at 1150° C and had barely perceptible flow at 1200° C. It remained smooth and glossy after cooling to room temperature.

Enamel B-11, containing the cobalt-iron spinel, flowed more than any of the other specimens and the surface blistered on cooling.

Enamel B-12, containing the cobalt-manganese spinel, flowed very slightly at 1150° and 1200° C but on cooling it blistered badly.

Enamel B-13, containing the cobalt-chromium spinel, flowed slightly in the 1100-1200° C range, and on cooling it had a smooth surface with some slightly mottled areas.

Since the B-9 enamel appeared to be capable of maintaining its properties to higher temperatures than the other enamels, its spectral emittance curves were determined over the range from 400° to 1150° C and the results are shown in Figure 7.

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1. J. C. Richmond and J. E. Stewart, "Spectral Emittance of Ceramic-Coated and Uncoated Specimens of Inconel and Stainless Steel", J. Am. Ceram. Soc. 42, 633-40 (1959).

2. W. N. Harrison, J. C. Richmond, E. K. Plyer, R. Stair, and H. K. Skramstad, "Standardization of Thermal Emittance Measurements", WADC Technical Report 50-51, August, 1959.

## B. REFLECTANCE AND EMITTANCE OF WHITE ENAMELS

Measurements were made of the total hemispherical reflectance at room temperature of white enamels opacified with ceric oxide, using magnesia, tin oxide, or zirconia as auxiliary opacifiers. The results are shown in Table II and Figure 8. At roughly comparable thicknesses (2-3 mils) the reflectances of Enamels W-1, W-3, and W-4 are not greatly different since the effect of the Inconel substrate has not been completely masked. There is some indication that a somewhat more reflective enamel is obtained by the combination of ceria and zirconia as opacifiers, than by the combination of ceria and stannic oxide. However, the latter (Enamel W-3) had the most satisfactory enameling characteristics and specimens were therefore prepared for determination of the total normal emittance at high temperatures. Values are given in Figure 9 for temperatures of 400, 600, and 800° C.

Spectral emittance curves of the W-3 enamel at temperatures of 600 and 950° C were determined and are shown in Figure 10.

# IV. SUMMARY

We feel that a considerable improvement has been made in the development of Enamel B-9 over coatings that were available previously for providing Inconel with reproducible emissivity characteristics as well as protection against oxidation at high temperatures. This enamel, which is opacified with a black nickel-iron spinel, shows good adherence and fit to Inconel and it undergoes barely perceptible flow on being subjected to a temperature of 1200° C (2190° F).

The emittance characteristics of the B-9 enamel approximate those of heavily oxidized Inconel at corresponding temperatures and wavelengths. However, coating of the metal with the enamel has the advantage that a smooth surface is preserved and the scaling and flaking, which occurs with continued oxidation of the Inconel, is prevented.

In the case of the white enamel, W-3, the requirement that the coating possess high emittance in the infrared to temperatures of 700° C or greater is very adequately fulfilled. In general, the spectral emittance curves resemble fairly closely those obtained by the National Bureau of Standards for a somewhat similar enamel, except that our curves show lower emittances than those reported by the Bureau at wavelengths greater than about 5 microns and somewhat higher emittances at wavelengths below 5 microns. The Bureau's enamel consisted of a frit somewhat similar to the one used in our formulations with ceric oxide as the opacifier. The opacifiers in our W-3 enamel were ceric oxide and stannic oxide, the purpose of the latter being to increase the reflectivity of the enamel. Continued experimentation with opacifiers would

## TABLE II

### TOTAL HEMISPHERICAL REFLECTANCE OF WHITE ENAMELS AT ROOM TEMPERATURE

| Wavelength Microns | W-1 3.1 Mils | W-3 2 Mils | W-3 6.0 Mils | W-4 2.4 Mils |
|---|---|---|---|---|
| 2.60 | 0.53 | 0.41 | 0.62 | 0.53 |
| 2.30 | 0.53 | 0.41 | 0.63 | 0.53 |
| 2.00 | 0.54 | 0.42 | 0.63 | 0.54 |
| 1.70 | 0.55 | 0.43 | 0.64 | 0.54 |
| 1.40 | 0.56 | 0.45 | 0.65 | 0.57 |
| 1.10 | 0.57 | 0.47 | 0.67 | 0.59 |
| 0.80 | 0.58 | 0.49 | 0.67 | 0.61 |
| 0.50 | 0.55 | 0.52 | 0.66 | 0.62 |
| 0.45 | 0.51 | 0.53 | 0.65 | 0.61 |
| 0.42 | - | 0.54 | - | 0.57 |

### Compositions

W-1: 60 parts Frit 332; 30 parts $CeO_2$; 10 parts MgO

W-3: 60 parts Frit 332; 20 parts $CeO_2$; 20 parts $SnO_2$

W-4: 60 parts Frit 332; 20 parts $CeO_2$; 20 parts $ZrO_2$

undoubtedly make possible an increase in the total hemispherical reflectance of the enamel at room temperature to higher values than the maximum of 0.7 obtained for the W-3 formulation.

The work reported herein was carried out under a contract with the Materials Central, Wright Air Development Division. Spectral emissivity measurements were made under a contract with Air Force Cambridge Research Center. Experimental work on the project was performed by D. G. Burgess, J. R. Jasperse, W. S. Martin, and R. M. Cornish of the staff of Arthur D. Little, Inc.

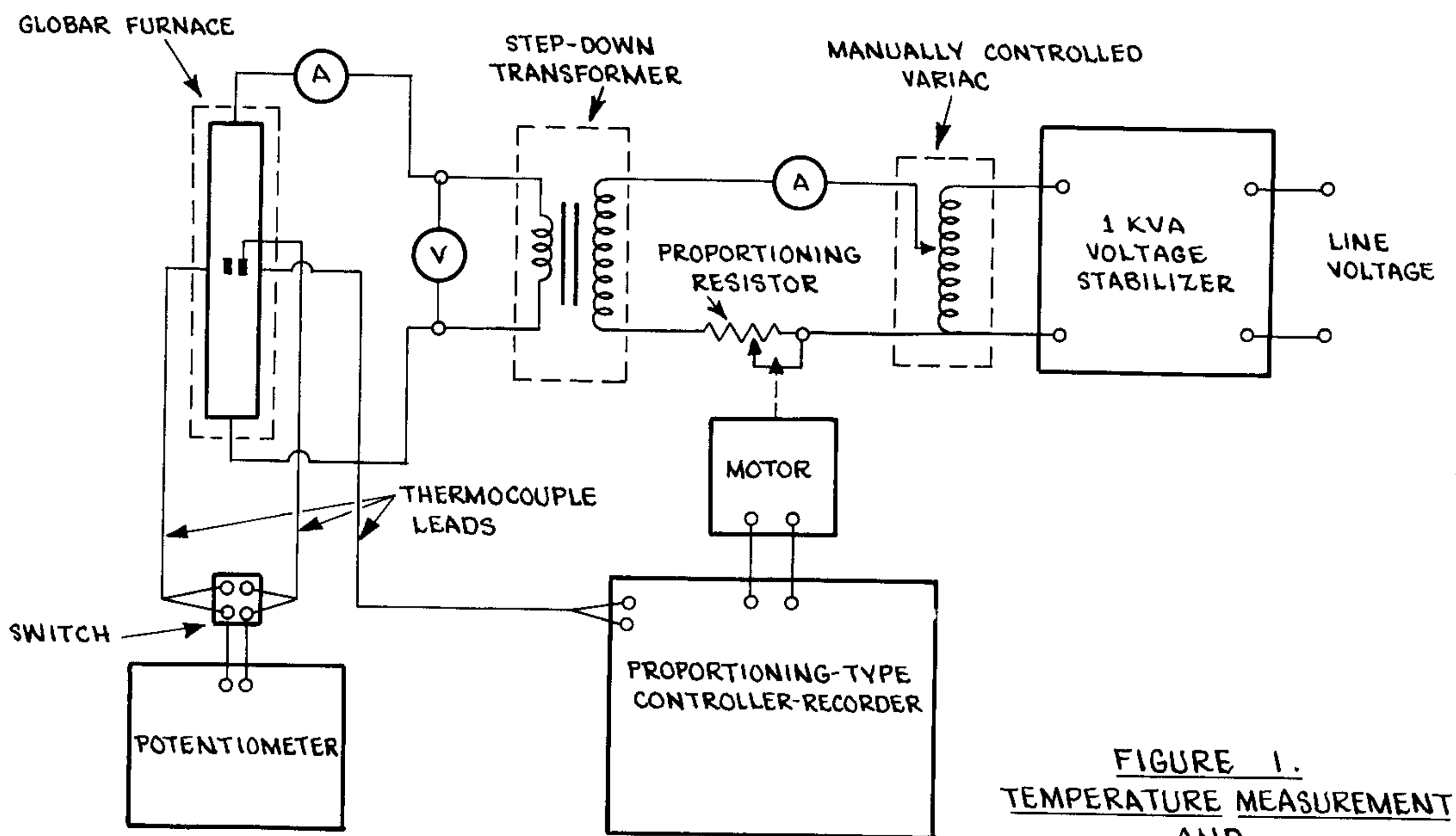


FIGURE 1.
TEMPERATURE MEASUREMENT
AND
CONTROL NETWORK

Figure 1 Temperature Measurement and Control Network

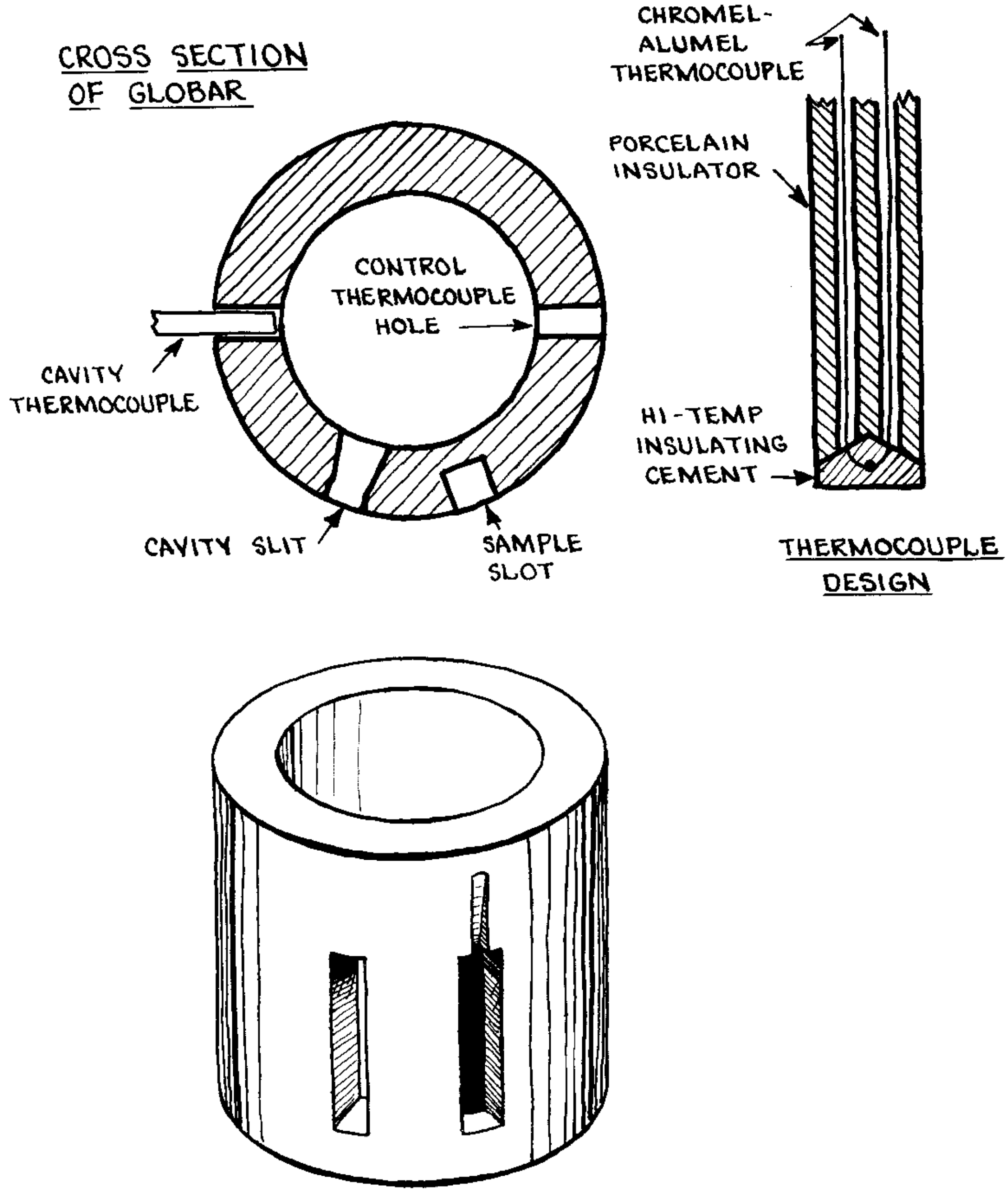


FIGURE 2.
HOLLOW CYLINDRICAL GLOBAR HEATING ELEMENT

Figure 2 Hollow Cylindrical Globar Heating Element

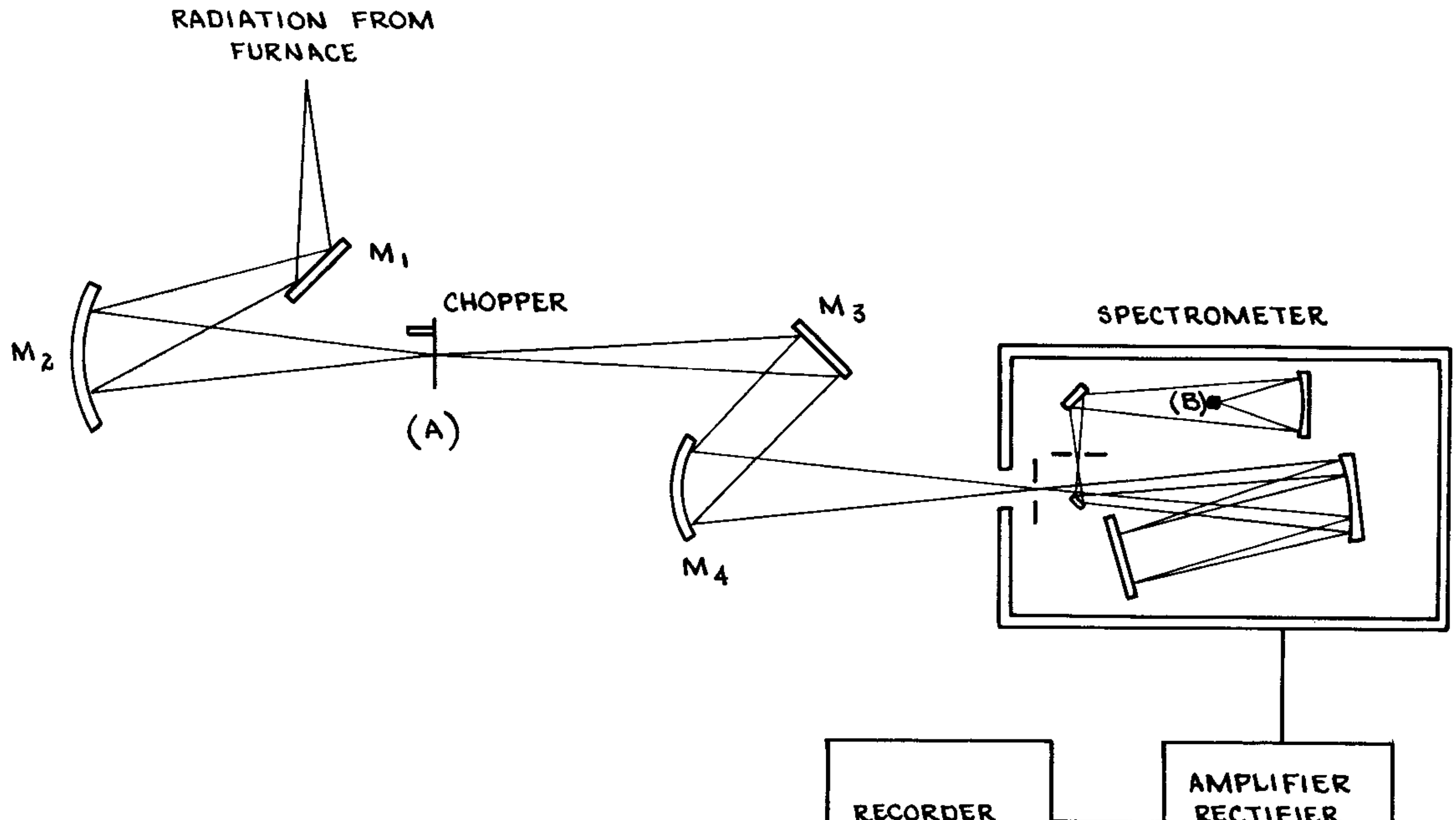


FIGURE 3.
RADIATION DETECTION SYSTEM

Figure 3 Radiation Detection System

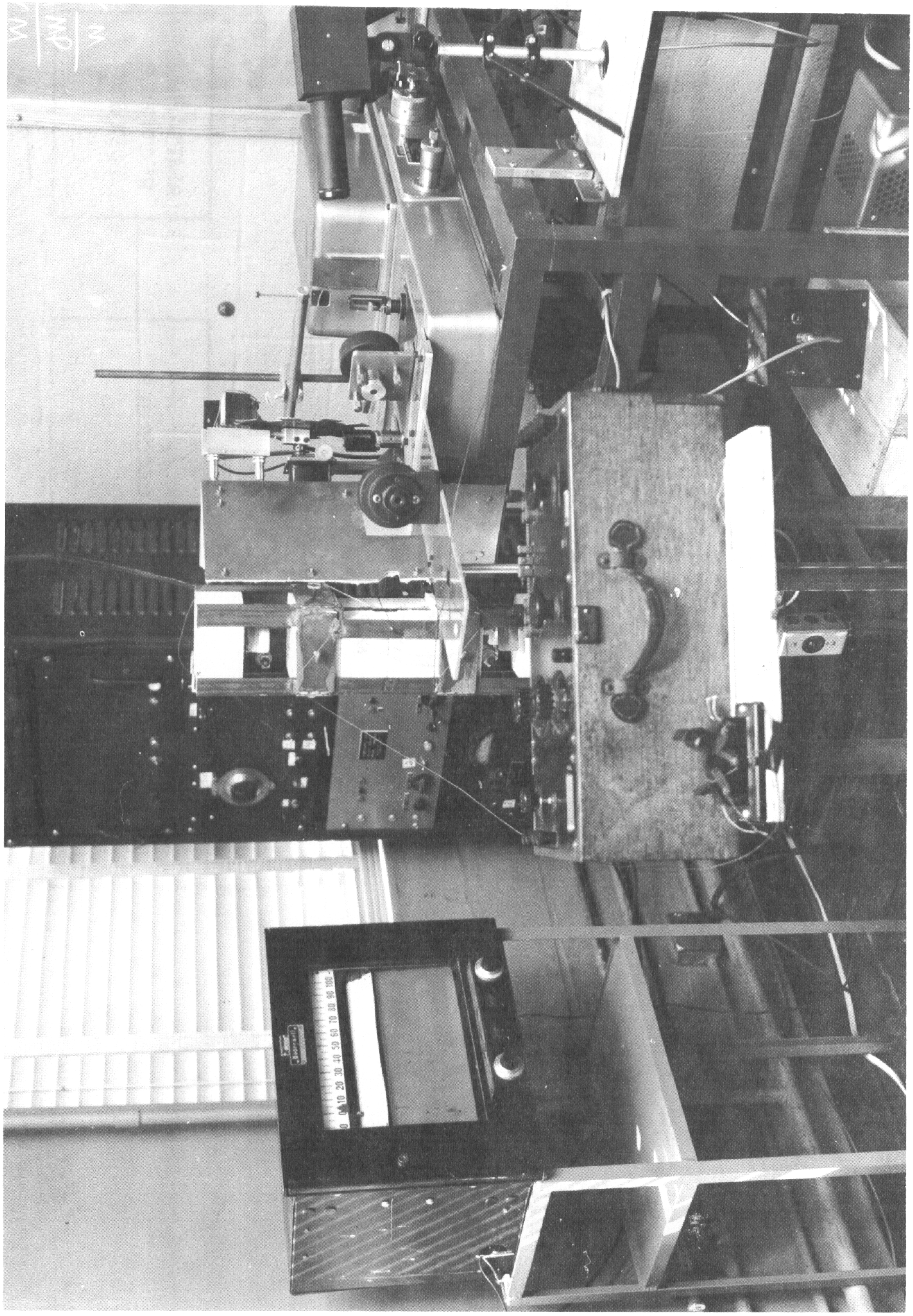

Fig. 4 Equipment for measuring high-temperature emittance.

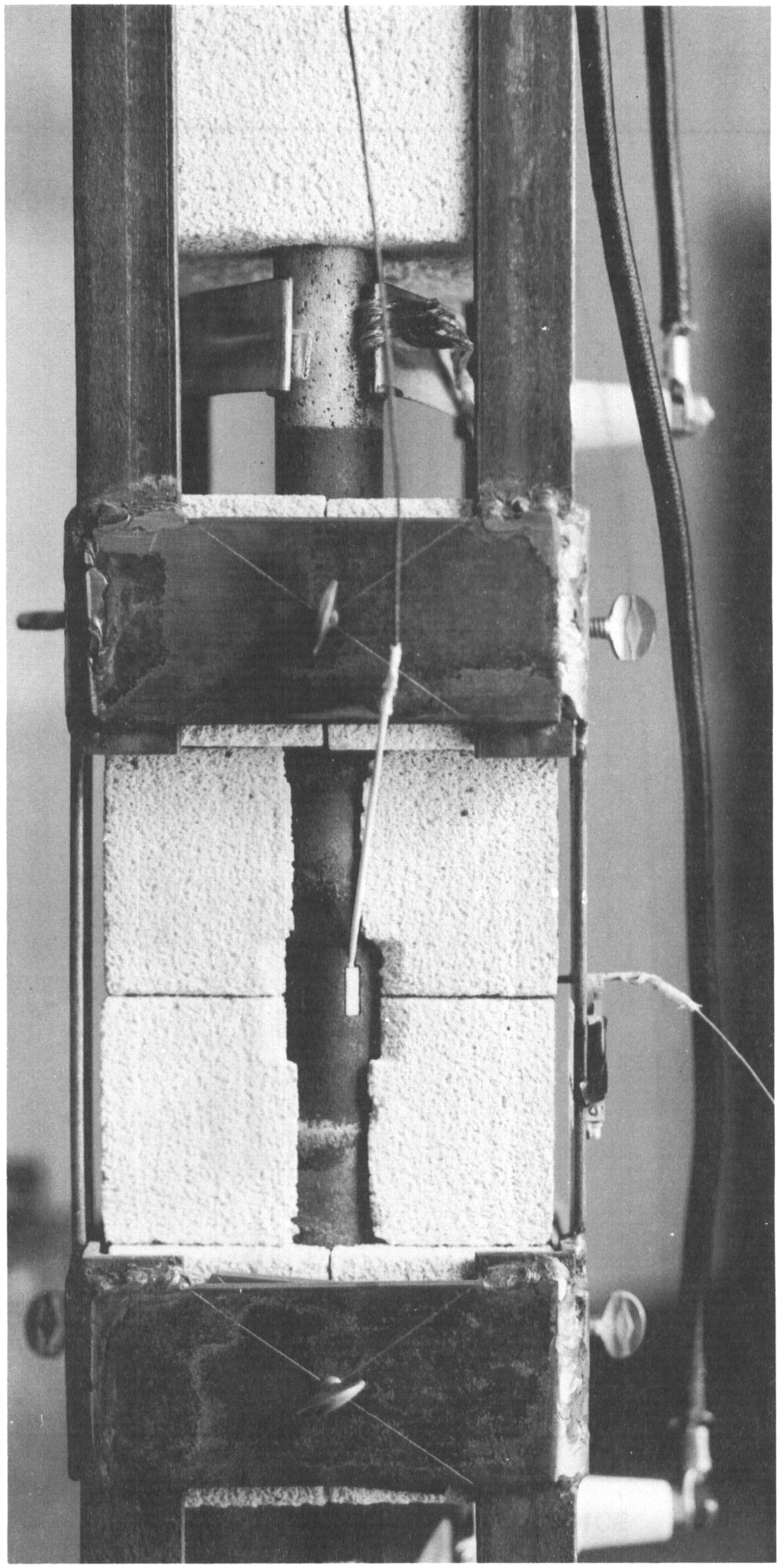

Fig. 5 Hollow globar furnace showing enameled specimen in place.

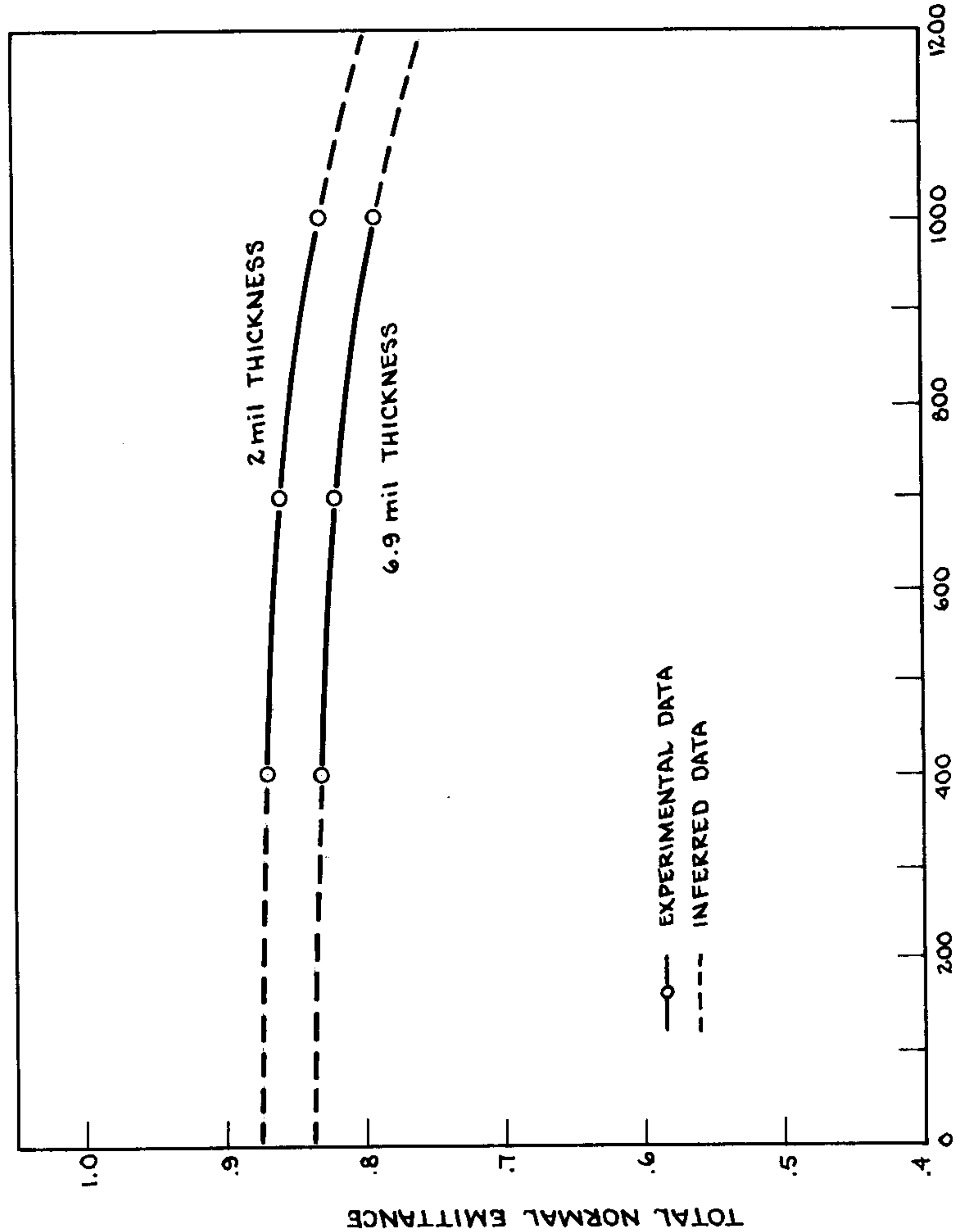


Figure 6 Total Normal Emittance of Enamel B-12

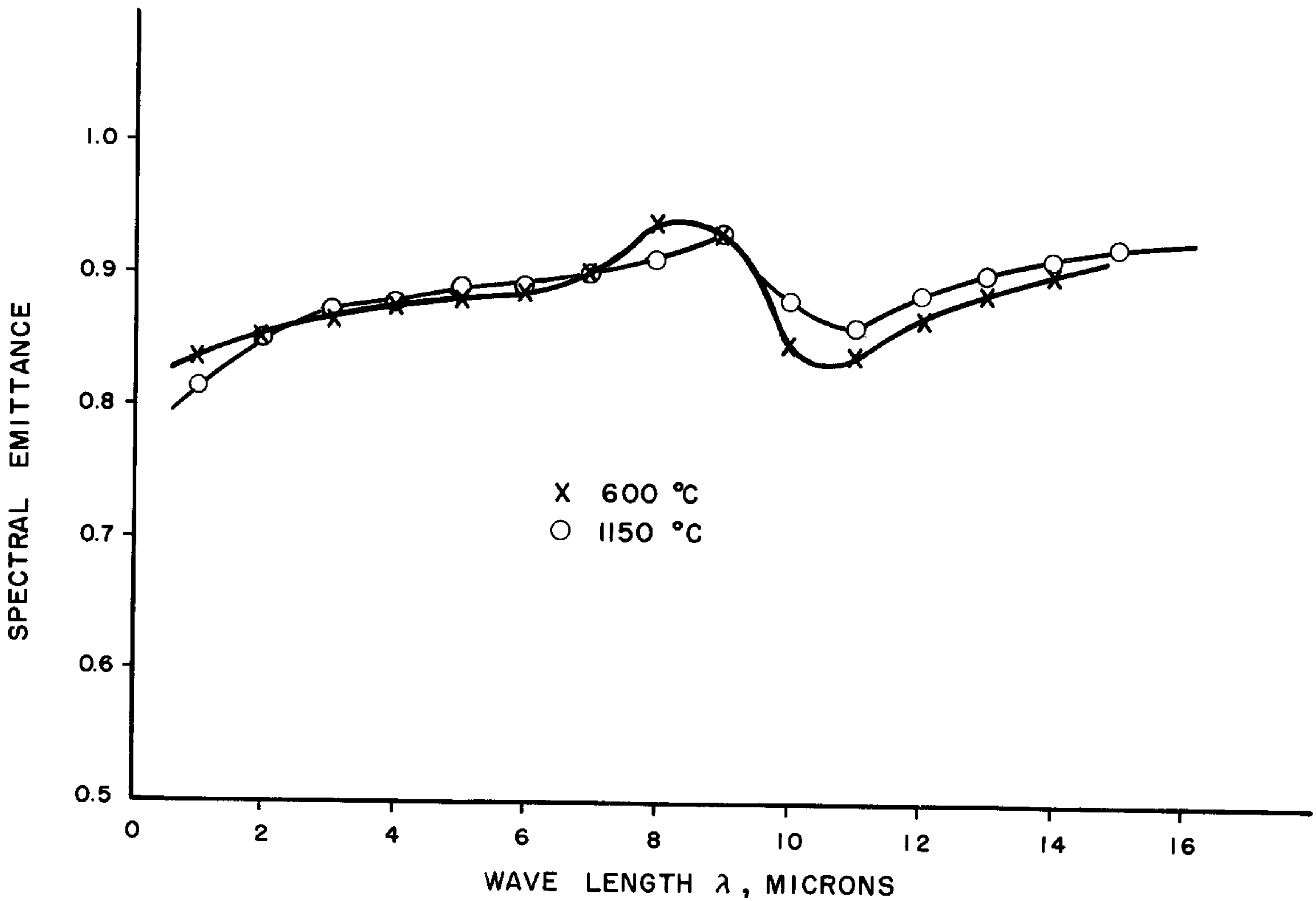


Figure 7 Spectral Emittance Curves for Enamel B-9 (2-Mil Thickness) on Inconel

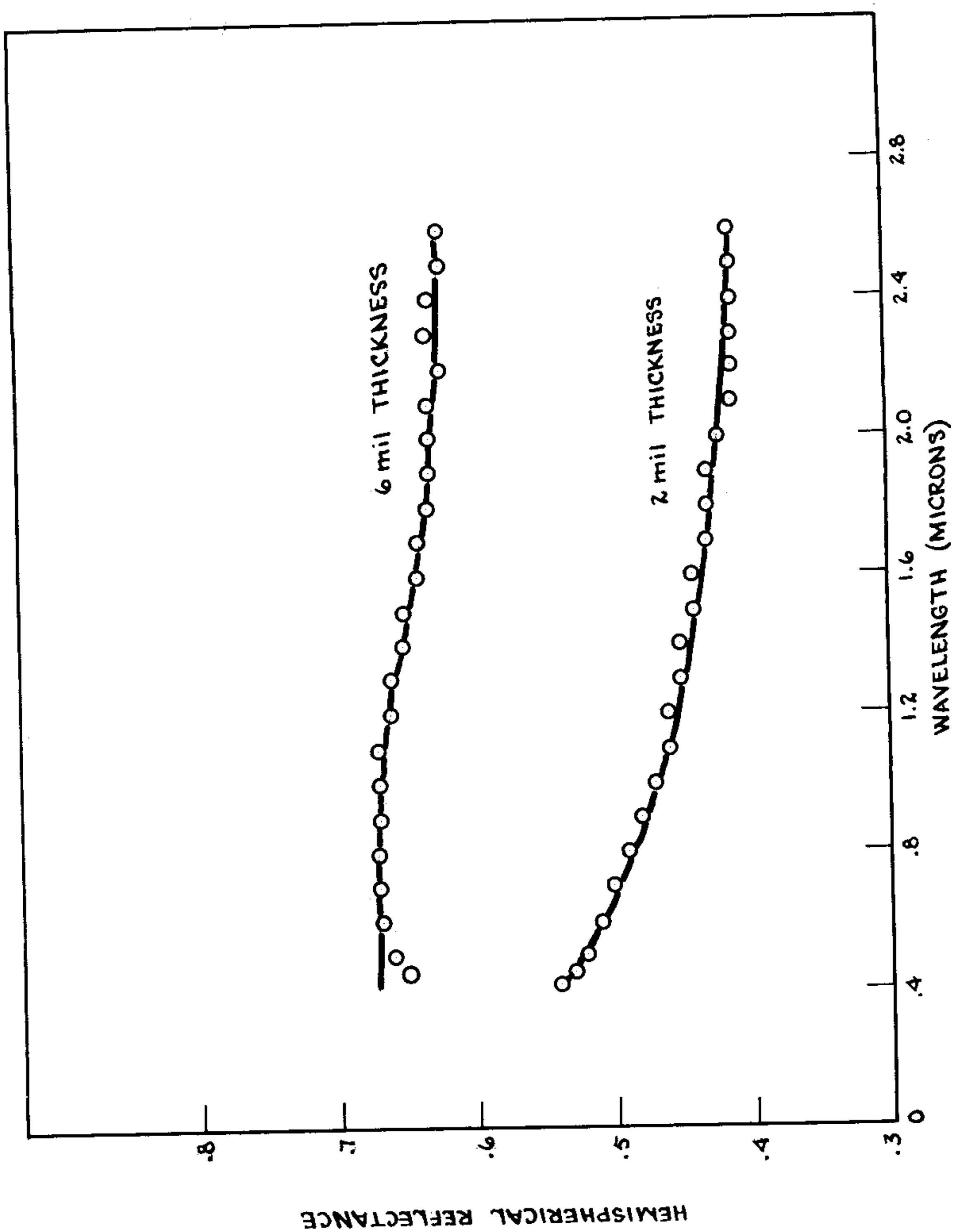


Figure 8 Hemispherical Reflectance of Enamel W-3 at Room Temperature

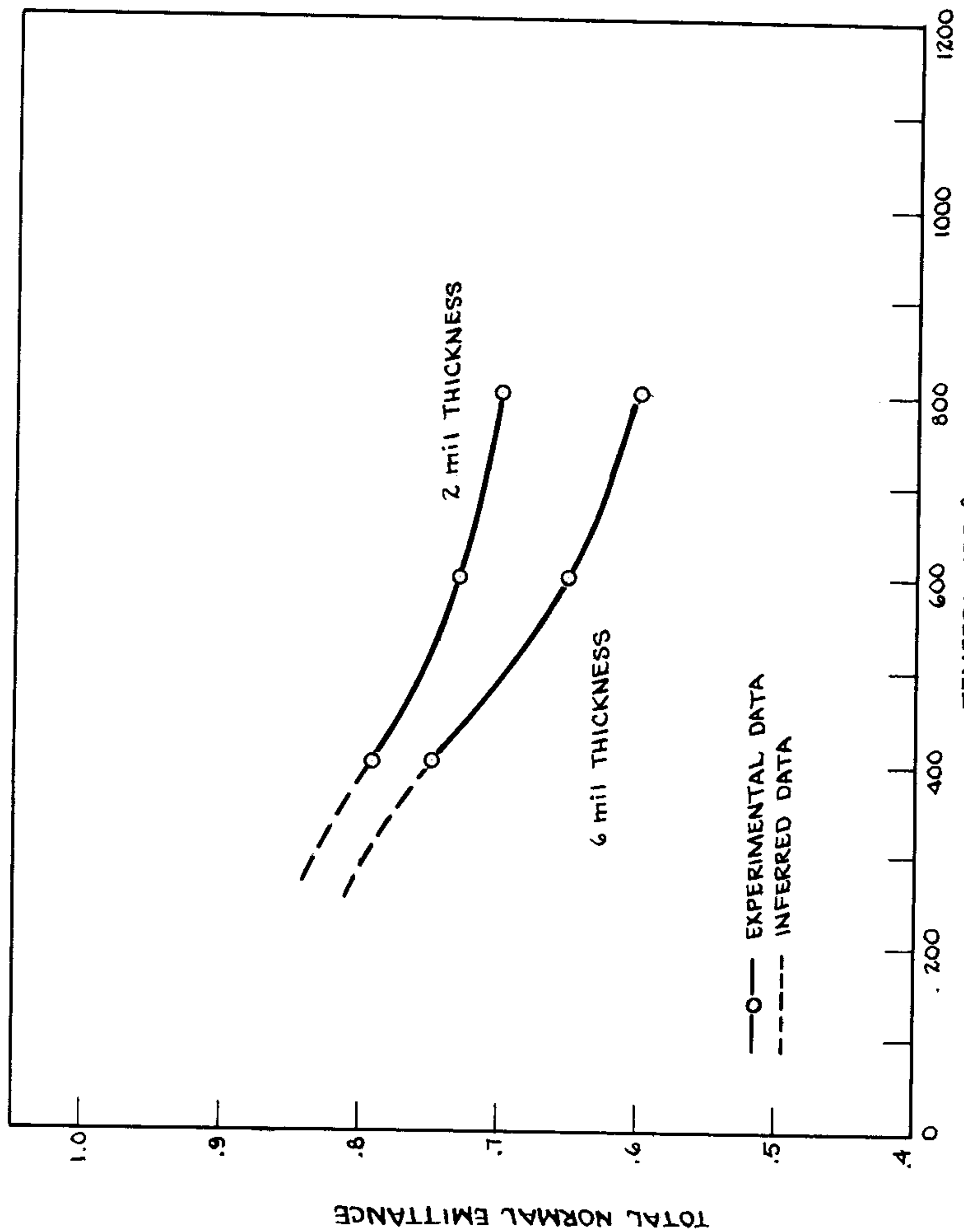


**Figure 9 Total Normal Emittance of Enamel W-3**

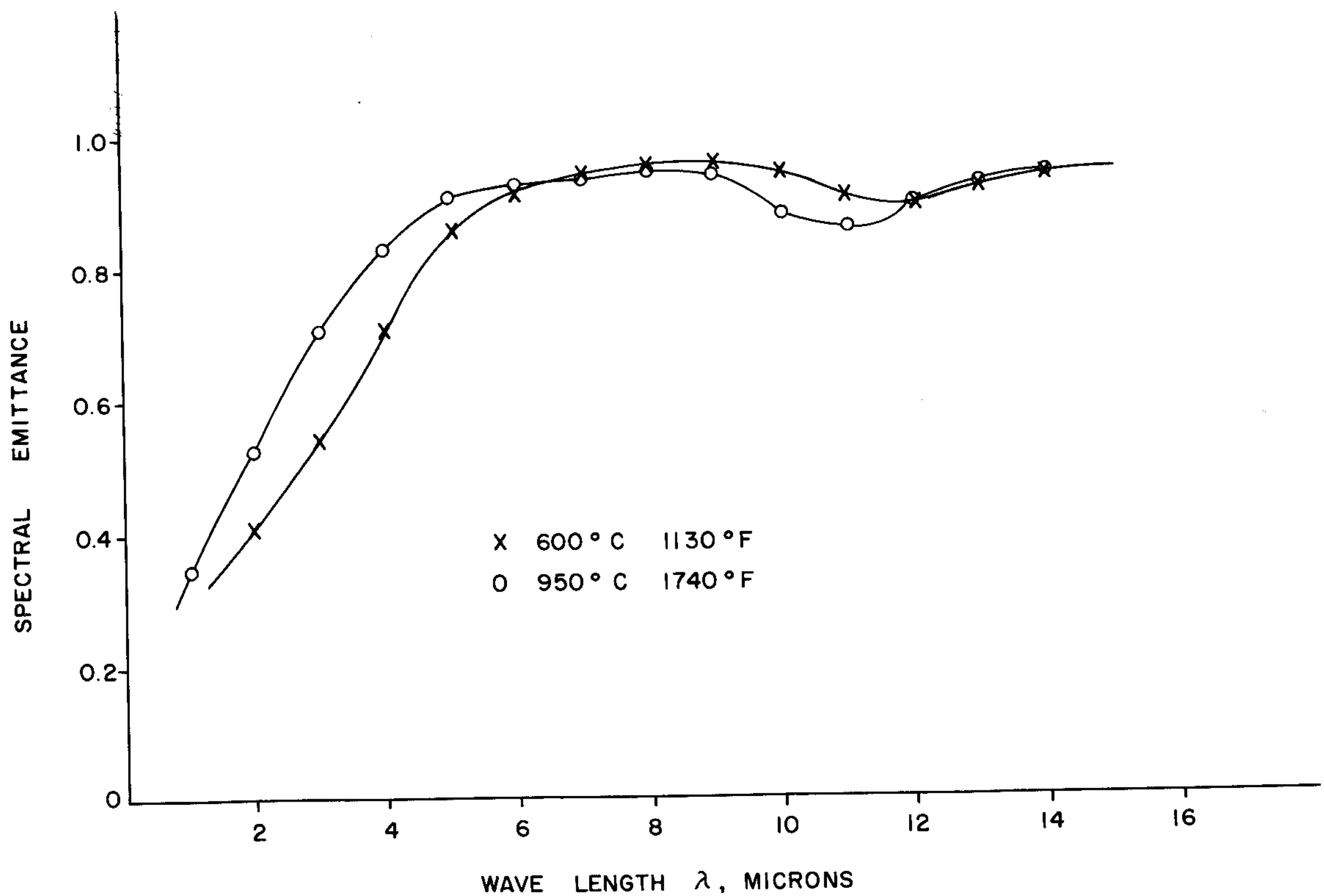


Figure 10 Spectral Emittance for Enamel W-3 (5-Mil Thickness) on Inconel